

# 1. Basic Statistical Mechanics

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## Probability and Statistics

Explain the meaning of probability. Calculate probabilities and averages for simple examples.

Explain how number of particles at each energy level depends on probability.

Use Boltzmann distribution to calculate number of particles at each energy level.

Use Boltzmann distribution to calculate total energy.

## 1

### Balls in a bag.

Suppose there are 10 balls in bag: 3 red, 7 blue. If I pick a ball at random, would it be red or blue?

We don't know. But we know that if I pick a ball 10 times (replacing it each time), then 3 out of 10 times it would be red. 7 out of 10 times it would be blue. Roughly.

This idea is quantified by the definition of probability:

probability of an event =  $\frac{\text{number of possible outcomes for that event}}{\text{total number of possible outcomes}}$ .

So

$$\text{probability of red ball} = \frac{3}{10},$$

$$\text{probability of blue ball} = \frac{7}{10}.$$

If I pick and replace the ball 100 times, I would get red balls approximately

$$\frac{3}{10} \times 100 = 30$$

times. Approximately, but most likely a bit more or a bit less.

So if I say 3/10 of the times I get red, then there is some error in this statement.

In reality, I might get 29 red balls, or 33 red balls, or some other random numbers of red balls. But chances are, it would not be too far from 30. It can be proven that if you repeat the experiment many times, the average of all the numbers of red balls that you picked each time would approach 30.

If I pick and replace the ball 100 times, and I say that 3/10 of the times I get red, then my error is about  $1/\sqrt{100}$  which is 10%.

But if I pick and replace the ball  $10^{24}$  times, and I say that 3/10 of the times I get red, then the error is only  $1/\sqrt{10^{24}}$ . This is so small that I can neglect the error and treat 3/10 as an accurate answer.

Why would I even think about picking a ball  $10^{24}$  times from a bag?

Because  $10^{24}$  is close to the Avogadro constant  $6.022 \times 10^{23}$ , the typical number of atoms in any object that we would pick up - a cup of tea, an apple, or a piece of cake.

We call 3/10 the expected value of the proportion of red balls. In some sense, it is an average.

It is often convenient just to think of 3/10 as the proportion of red balls we would get, as long as we remember that it is an average, and the actual number could be different. Since the actual proportion takes a range of random values, we can think in terms of the standard deviation  $\sigma$ .

$\sigma$  is a kind of average of the difference between a random variable and its expected value (or mean). We may think of it as a measure of the error of an observed quantity.

It has been shown in statistics that  $\sigma$  gets smaller as the number  $N$  of of times I pick and replace the ball gets larger. In fact, the error in the proportion goes as  $1/\sqrt{N}$ .

There is a connection between the number of times I pick a ball from a bag, and the number of atoms in an object.

We know from quantum mechanics that the atoms and electrons have energies at discrete levels. If we can somehow know the probability of the particles at each level, then we can calculate the expected value of the total energy of the particles. Because the number of atoms is so large, the error would be negligible.

Once we know the total energy of the particles in a body, many thermodynamic properties can be calculated.

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## Statistical Mechanics

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Microstate

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At another point in time, the energy of each atom could have changed. The 10 atoms would have a different arrangement in energy levels. This is possible as long total energy is conserved. This new arrangement would be a different microstate.

Which of these microstates is more likely? We will never really know. However, physicists made a very good guess: They assumed that all the microstates are equally likely.

By making this assumption, they calculated the thermodynamic properties of many things. The answers agreed well with experiments, so physicists are now convinced that this assumption is correct. They even promoted it to a principle:

“The principle of a priori probability.”

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## Statistical Mechanics

Suppose that a solid body contains 10 atoms, and each atom has 2 energy levels: the lower level  $\varepsilon_1$  and higher level  $\varepsilon_2$ . At a certain temperature, an atom can either be at  $\varepsilon_1$  or  $\varepsilon_2$ .

The atoms interact with each other through electromagnetic fields. Each atom can gain or lose some energy to another atom, and change from one level to the other.

At a particular point in time, each atom is at a particular energy level  $\varepsilon_1$  or  $\varepsilon_2$ . So the 10 atoms have a particular arrangement in energy levels. This arrangement is called a **microstate**.

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Macrostate

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We want to know the number of atoms at each energy level ( $\varepsilon_1, \varepsilon_2$ ). Once we know this, we can calculate the total energy of the body, and other thermodynamic properties.

Suppose that the numbers are  $(n_1, n_2)$ . This set of numbers of atoms at different levels is called a **macrostate**.

Each macrostate can correspond to different microstates. For example, if the macrostate is  $(7, 3)$ , it means that 7 atoms are at  $\varepsilon_1$  and 3 atoms are at  $\varepsilon_2$ . However, the 3 atoms at  $\varepsilon_2$  can be any of the 10 atoms.

For each macrostate, there are different arrangements, or microstates. We can find the number of different microstates using the mathematics of combinations and permutations.

Lets calculate the number of arrangements (microstates) for the macrostate (7, 3). Since 7 atoms are at  $\varepsilon_1$  and 3 atoms are at  $\varepsilon_2$ , the answer is

$$\Omega = \frac{10!}{7!3!}.$$

We can generalise this. Let the total number of atoms be  $N$ , and the macrostate be  $(n_1, n_2)$ . Then the number of microstates in this macrostate is

$$\Omega = \frac{N!}{n_1!n_2!}.$$

We can then extend this to any number of energy levels. Suppose that the macrostate is  $(n_1, n_2, n_3, \dots)$ , with  $n_1$  atoms at level 1,  $n_2$  at level 2,  $n_3$  at level 3, and so on. Then the number of microstates is

$$\Omega = \frac{N!}{n_1!n_2!n_3!\dots}.$$

The Boltzmann distribution can be obtained using these assumptions:

1. The number of particles (atoms) is constant.
2. The total energy or temperature is constant.
3. Each microstate is equally likely (as long as it obeys 1 and 2).
4. The positions of the atoms are fixed (so they are distinguishable - we can tell one from another).
5. The number of particles is very large.
6. Boltzmann's postulate for entropy:  $S = k_B \ln \Omega$ , where  $\Omega$  is the number of microstates for a particular macrostate.

Detailed derivation is available in previous years' lecture notes.

Since we assume that each microstate is equally likely, we can then find the probability of each macrostate:

$$\text{probability of } (n_1, n_2) = \frac{\text{number of possible microstates for } (n_1, n_2)}{\text{total number of possible microstates}}$$

We want to find the macrostate  $(n_1, n_2)$  with the highest probability. When the number of atoms is very large (e.g.  $10^{24}$ ), this macrostate is given by this formula:

$$n_i = A \exp(-\varepsilon_i/k_B T)$$

where  $i = 1, 2$ .

This is called the Boltzmann distribution.

The factor  $\exp(-\varepsilon_i/k_B T)$  is called Boltzmann factor.

A brief note about Boltzmann's postulate for entropy

$$S = k_B \ln \Omega.$$

This is a formula postulated by Ludwig Boltzmann.

The concept of entropy was developed by Rudolf Clausius around 1850s. The entropy change of a system is related to the heat input  $dQ$  by

$$dS = \frac{dQ}{T}.$$

It is a mathematical concept useful for calculating heat changes. At first, its connection to atoms was not known.

Then in 1870s, Boltzmann proposed his postulate. This was used to derive the Boltzmann distribution, which agreed well with experiments.

In this way, Boltzmann provided the microscopic explanation for entropy - in terms of  $\Omega$ , the number of microstates for a particular macrostate.

The examples so far are about atoms with two energy levels.

$$n_i = A \exp(-\varepsilon_i/k_B T).$$

The Boltzmann distribution also applies to particles with any number of energy levels, so that  $i = 1, 2, 3, \dots$

We are mainly interested in the total number of particles and the total energy. These are related to the number  $n_i$  of particles at each energy level.

The total number is the sum of particles at all levels:

$$N = n_1 + n_2 + n_3 + \dots = \sum_i n_i.$$

The Boltzmann distribution is true for a number of systems, such as:

- atoms in a solid, and
- particles in an ideal gas.

If is not true for some systems, e.g.:

- electrons in metals, and
- atoms at extremely low temperatures.

In the last two cases, the distributions are different. We shall learn more about these distributions later on.

For the total energy, there are  $n_1$  atoms at level  $\varepsilon_1$ , so the energy at level 1 is  $n_1\varepsilon_1$ . Likewise for level 2, and so on.

The total energy is the sum of energies at all levels:

$$U = n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \dots = \sum_i n_i\varepsilon_i.$$

Note that the number  $n_i$  given by Boltzmann distribution

$$n_i = A \exp(-\varepsilon_i/k_B T).$$

is an expected value, just like the expected number of red balls when you pick 10 balls from a bag with red and blue balls.

This means that at different points in time,  $n_i$  could change. This means there is some error in the above formula. However, we know that the percentage error goes as  $1/\sqrt{N}$ , where  $N$  here is the total number of particles.

Since  $N$  is about  $10^{24}$  for typical objects, the percentage error is extremely small, and we usually neglect this.

**Exercise 1**

How many atoms are there in each of the following?

$$(N_A = 6.022 \times 10^{23})$$

- 1) 1 mole of iron
- 2) 0.2 mole of copper
- 3) 3 moles of silver
- 4) 1 mole of oxygen ( $O_2$ ), and how many molecules?
- 5) 1 mole of water ( $H_2O$ ), and how many oxygen atoms?
- 6) 1 mole of sodium chloride ( $NaCl$ ), and how many sodium ions?
- 7) 1 mole of helium-4 ( $^4He$ )
- 8) 1 mole of helium-3 ( $^3He$ )

**Exercise 2**

What is the mass of each of the following? ( $A_r$  stands for relative atomic mass.)

- 1) 1 mole of iron ( $A_r=56$ )
- 2) 0.2 mole of copper ( $A_r=64$ )
- 3) 3 moles of silver ( $A_r=108$ )
- 4) 1 mole of oxygen ( $O_2$ ) ( $A_r=16$ )
- 5) 1 mole of water ( $H_2O$ ) ( $A_r$  of  $H=1$ , of  $O=16$ )
- 6) 1 mole of sodium chloride ( $NaCl$ ) ( $A_r$  of  $Na=23$ , of  $Cl=35.5$ )
- 7) 1 mole of helium-4 ( $^4He$ )
- 8) 1 mole of helium-3 ( $^3He$ )

**Solutions to Exercise 1**

- 1)  $6.022 \times 10^{23}$
- 2)  $0.2 \times 6.022 \times 10^{23}$
- 3)  $3 \times 6.022 \times 10^{23}$
- 4)  $2 \times 6.022 \times 10^{23}$  atoms, and  $0.2 \times 6.022 \times 10^{23}$  molecules
- 5)  $3 \times 6.022 \times 10^{23}$  atoms, and  $6.022 \times 10^{23}$  oxygen atoms
- 6)  $2 \times 6.022 \times 10^{23}$  atoms, and  $6.022 \times 10^{23}$  sodium ions
- 7)  $6.022 \times 10^{23}$
- 8)  $6.022 \times 10^{23}$

**Solutions to Exercise 2**

- 1) 56 g
- 2)  $0.2 \times 64$  g
- 3)  $3 \times 108$  g
- 4)  $2 \times 16$  g
- 5)  $(2 \times 1 + 16)$  g
- 6)  $(23 + 35.5)$  g
- 7) 4 g
- 8) 3 g

**Exercise 3**

How many atoms are there in each of the following? ( $A_r$  stands for relative atomic mass.)

- 1) 1 g of iron ( $A_r=56$ )
- 2) 1 g of copper ( $A_r=64$ )
- 3) 1 g of silver ( $A_r=108$ )
- 4) 1 g of oxygen ( $O_2$ ) ( $A_r=16$ )
- 5) 1 g of water ( $H_2O$ ) ( $A_r$  of H=1, of O=16)
- 6) 1 g of sodium chloride (NaCl) ( $A_r$  of Na=23, of Cl=35.5)
- 7) 1 g of helium-4 ( $^4He$ )
- 8) 1 g of helium-3 ( $^3He$ )

**Exercise 4**

A system of particles is at a temperature of 2 K. Find the Boltzmann factor for each of these energy levels:

( $k_B = 1.38 \times 10^{-23}$ )

- 1)  $1 \times 10^{-23}$  J
- 2)  $2 \times 10^{-23}$  J
- 3)  $3 \times 10^{-23}$  J
- 4)  $4 \times 10^{-23}$  J
- 5)  $5 \times 10^{-23}$  J
- 6)  $6 \times 10^{-23}$  J
- 7)  $7 \times 10^{-23}$  J
- 8)  $8 \times 10^{-23}$  J

**Solutions to Exercise 3**

- 1)  $1/56 \times 6.022 \times 10^{23}$
- 2)  $1/64 \times 6.022 \times 10^{23}$
- 3)  $1/108 \times 6.022 \times 10^{23}$
- 4)  $1/(2 \times 16) \times 6.022 \times 10^{23}$
- 5)  $1/(1 + 1 + 16) \times 6.022 \times 10^{23}$
- 6)  $1/(23 + 35.5) \times 6.022 \times 10^{23}$
- 7)  $1/4 \times 6.022 \times 10^{23}$
- 8)  $1/3 \times 6.022 \times 10^{23}$

**Solutions to Exercise 4**

- 1) 0.6961
- 2) 0.4845
- 3) 0.3372
- 4) 0.2347
- 5) 0.1634
- 6) 0.1137
- 7) 0.07916
- 8) 0.05510

**Exercise 5**

There are  $10^{23}$  particles. The system has two energy levels only: 0 J and  $10^{-23}$  J. Find the number of particles at 0 J when the temperature is:

- 1) 1 K
- 2) 2 K
- 3) 3 K
- 4) 4 K
- 5) 5 K
- 6) 6 K
- 7) 7 K
- 8) 8 K

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**Worked Examples**

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**Solutions to Exercise 5**

- 1)  $6.736 \times 10^{22}$
- 2)  $5.896 \times 10^{22}$
- 3)  $5.601 \times 10^{22}$
- 4)  $5.452 \times 10^{22}$
- 5)  $5.362 \times 10^{22}$
- 6)  $5.302 \times 10^{22}$
- 7)  $5.259 \times 10^{22}$
- 8)  $5.226 \times 10^{22}$

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**Worked example**

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**Example 1**

There is one mole of atoms at a temperature of 1 K. Each atom has energy levels  $-10^{-23}$  J and  $10^{-23}$  J. Find the number of atoms at each level.

**Solution**

The formula is Boltzmann distribution

$$n_i = A \exp(-\varepsilon_i/k_B T).$$

Given

$$\varepsilon_1 = -10^{-23} \text{ J}, \varepsilon_2 = 10^{-23} \text{ J}, \text{ and } T = 1 \text{ K}.$$

We also know that  $n_1 + n_2 = N_A$  (Avogadro constant).

We need to find the numbers  $n_1$  and  $n_2$ . But what is  $A$ ?

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Lets write out all equations:

$$n_1 + n_2 = N_A$$

$$n_1 = A \exp(-\varepsilon_1/k_B T)$$

$$n_2 = A \exp(-\varepsilon_2/k_B T)$$

There are three unknowns:  $n_1$ ,  $n_2$  and  $A$ . Divide the last two equations:

$$\frac{n_1}{n_2} = \exp((\varepsilon_2 - \varepsilon_1)/k_B T).$$

Let this above fraction be  $r$ . So the total is  $N_A$  is divided into the ratio  $r : 1$ . Therefore

$$n_1 = \frac{r}{r+1} \times N_A = 4.876 \times 10^{23}$$

$$n_2 = \frac{1}{r+1} \times N_A = 1.145 \times 10^{23}$$

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### Worked example

#### Example 3

Following from the previous example, find the probability that an atom is at level 1, and the probability that it is at level 2.

#### Solution

The total number of atoms is  $N_A$ .

There are  $n_1$  atoms at level 1 and  $n_2$  atoms at level 2.

An atom can change level with time. So any one time, probability that it is at level 1 is

$$\frac{\text{number of possible atoms at level 1}}{\text{total number of atoms}} = \frac{n_1}{N_A} = \frac{4.876 \times 10^{23}}{6.022 \times 10^{23}}$$

Probability that it is at level 2 is

$$\frac{\text{number of possible atoms at level 2}}{\text{total number of atoms}} = \frac{n_2}{N_A} = \frac{1.145 \times 10^{23}}{6.022 \times 10^{23}}$$

#### Example 2

Following from the previous example, find the total energy of the atoms.

#### Solution

There are  $n_1$  atoms with energy  $\varepsilon_1$ , so the energy of these atoms is  $n_1 \varepsilon_1$

There are  $n_2$  atoms with energy  $\varepsilon_2$ . so the energy of these atoms is  $n_2 \varepsilon_2$ .

Therefore the total energy is

$$U = n_1 \varepsilon_1 + n_2 \varepsilon_2.$$

Using the values from the previous example, we get

$$U = (4.876 \times 10^{23})(-10^{-23}) + (1.145 \times 10^{23})(10^{-23}) = 6.021 J.$$

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### Worked example

#### Example 4

There are a number of atoms at a temperature of 1 K. Each atom has energy levels  $-10^{-23}$  J and  $10^{-23}$  J. Find the probability that an atom is at each level.

#### Solution

This time, we are not given the total number of particles. We still have the Boltzmann distribution:

$$n_1 = A \exp(-\varepsilon_1/k_B T)$$

$$n_2 = A \exp(-\varepsilon_2/k_B T)$$

but we cannot find  $A$  if we don't know the the total number of particles.

But we know that the probability that an atom is at level 1 is

$$\frac{\text{number of possible atoms at level 1}}{\text{total number of atoms}} = \frac{n_1}{n_1 + n_2}$$

If we substitute the Boltzmann distribution,  $A$  cancels out!

$$\frac{n_1}{n_1 + n_2} = \frac{A \exp(-\varepsilon_1/k_B T)}{A \exp(-\varepsilon_1/k_B T) + A \exp(-\varepsilon_2/k_B T)}$$

We do know the energy levels and temperature, so we can not calculate this. In the same way, the probability that an atom is at level 2 is

$$\frac{n_2}{n_1 + n_2} = \frac{A \exp(-\varepsilon_2/k_B T)}{A \exp(-\varepsilon_1/k_B T) + A \exp(-\varepsilon_2/k_B T)}$$

The answers are 4.876/6.022 and 1.145/6.022 respectively.